CYCLIC 1,2-DIKETONES: STRUCTURE AND SPECTRA OF THE DIBENZAL DERIVATIVES

BY

GENE CONRAD ROBINSON

Ph.B., University of Chicago, 1947
M.S., University of Chicago, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

The observations of Karrer and his coworkers on the ultraviolet absorption spectra of the polyene diketones indicated that the 1,2-diketone unit is an insulating group.[1] The work of Leonard and his coworkers on the benzils was consistent with this view but complicating factors in this series made the data inconclusive on the point in which we were interested.[2]

The point to be investigated was the variation in the insulating power of the dicarbonyl unit as the dicarbonyl angle is varied. The simplest readily available series, where the dicarbonyl angle might vary regularly and predictably, was the cyclic dibenzylidene-1,2-diketones. As many of these compounds as possible were to be prepared and an attempt made to correlate shifts in the intensity and wavelength of the absorption maxima with variations in the dicarbonyl angle as indicated by Fisher-Taylor-Hirschfelder models.

Discussion Of Results

The syntheses of 3,7-dibenzylidene-1,2-cycloheptanedione; 3,9-dibenzylidene-1,2-cyclononanedione; 3,10-dibenzylidene-1,2-cyclodecanedione and 3,11-dibenzylidene-1,2-cyclohendecanedione were successfully accomplished. In addition cinnamil was prepared for spectral comparison. These compounds were prepared by the reaction of benzaldehyde with the corresponding 1,2-diketones using piperidine as the catalyst.

The ultraviolet absorption spectra of the cyclic compounds were all closely similar in both wavelength and intensity of absorption. The spectra were similar to the absorption of 2-benzylidenecyclohexanone but the main peak was shifted 20 $m\mu$ to the red. This shift was attributed to the electrostatic

influence of the second carbonyl group. The peak in cinnamil was shifted *ca.* 45mμ to the red from that of benzalacetone. This shift was attributed to the ease with which cinnamil becomes coplanar in contrast to the cyclic compounds. The positions of the maxima were consistent with the assumption that the dicarbonyl unit is an insulating group.

The isomerization of the 3,7-dibenzylidene-1,2-cycloheptanedione to 3,7-dibenzyltropolone was successful and an investigation of the mechanism of the isomerization showed that hydrogen bromide was necessary for the reaction and that some step in the process was free radical in nature.[3] While preparing bromo compounds which were possible intermediates an alternative synthesis of the tropolone was found.

The reaction of benzaldehyde with 1,2-cyclohexanedione and with 1,2-cyclododecanedione led to anomalous products of doubtful structure. Preliminary investigations of these compounds were carried out and possible structures were postulated.

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VITA

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